INDO Calculation of the Fulminate–Cyanate Rearrangement

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Summary The INDO calculation of the fulminate–cyanate rearrangement indicates a cyclic intermediate.

BY heating carefully a suspension of potassium fulminate in a mull a rearrangement into potassium cyanate was observed by i.r. spectroscopy.[1] Also, nitrile oxides (RCNO)[2] and organometallic fulminates[3] isomerize neatly to isocyanates. We were interested to determine by calculation whether or not a rearrangement occurs *via* a cyclic transition state (or intermediate) with the structure (**1**). We describe the electronic structures, as obtained by

(1) 

LCAO–SCF–MO calculations, of the fulminate ion, the postulated oxazirine ion (**1**), and the cyanate ion. The atomic charges and π-bond orders of fulminate ion and cyanate ion have been reported using group-orbitals.[4] Recently the similar isocyanide–cyanide rearrangement was studied by use of the "extended Hückel method".[5] The calculation of the reaction path for simulated rearrangement is based on the INDO (intermediate neglect of differential overlap) method, described in detail by Pople, Beveridge, and Dobosh.[6] We assumed that during the rearrangement the oxygen atom moves on an elliptical curve (Figure 1), whereas the C–N co-ordinates remain unchanged. The geometry of the elliptical curve was deduced from the bond distances of the fulminate ion, the cyanate ion, and the oxazirine ion. The bond distances of the fulminate ion[1] and the cyanate ion[4] have been derived from the C–N, N–O, and C–O stretching force-constants. The y co-ordinate of the cyclic oxazirine ion has been estimated.

Figure 2 shows the total energy along the reaction co-ordinate x, the energy at each point being a minimum with respect to variation of y. The energy curve indicates a remarkable stabilization of the postulated intermediate (**1**). The calculated activation energies may not yet have The total antibonding two-centre interaction[10] between the carbon and the oxygen atoms indicates a linear structure of the fulminate ion. This agrees with the observed i.r. data.[1] A further significant feature of the postulated oxazirine ion is the almost uniform charge distribution.

TABLE 1. *Parameters used in INDO calculations*

Atom	Average I.P. for *s*-orbitals	Average I.P. for *p*-orbitals	Slater exponent	G^1 integrals	F^2 integrals	Molecule	Bond distances (Å) d_{C-N}	d_{N-O}	d_{C-O}
C	−14·051	−5·572	1·625	0·26771	0·17372	Fulminate	1·17	1·33	2·50
N	−19·3164	−7·275	1·950	0·34603	0·21906	Oxazirine	1·17	1·43	1·43
O	−25·3902	−9·11	2·275	0·43423	0·26642	Cyanate	1·17	2·40	1·23

TABLE 2. *Stretching force constants and results as given by INDO calculations*

	Stretching force constants (mdyne/Å)			Total two-centre contributions (ev)[10]			Bond-index[8]			Total electron density		
	k_{CN}	k_{NO}	k_{CO}	E_{total} (ev)	C–N	C–O	N–O	C–N	C–O	N–O	C	N	O
Fulminate	15·6[9,1]	6·81[9,1]		−956·0587	−58·5668	2·3782	−31·2623	2·77555	0·17724	1·03586	4·578	4·777	6·645
Oxazirine	—	—		−955·1771	−42·7714	−18·5109	−17·5613	2·08289	0·74795	0·78342	4·340	5·233	6·4372
Cyanate	15·9[9]		11·0[9]	−956·7144	−55·8540	−39·4028	2·3346	2·51042	1·42557	0·28884	3·709	5·637	6·654

chemical accuracy, which could depend on the fact that the INDO parameters (Table 1) are not sufficiently well balanced.[7]

The analysis of the bond-indices[8] and electron densities listed in Table 2 clearly confirms the results obtained from fulminate ion i.r. spectra,[1] which show that the fulminate ion can be described by the valence-bond formula $|\overline{C}\equiv\overset{+}{N}-\overline{O}|$.

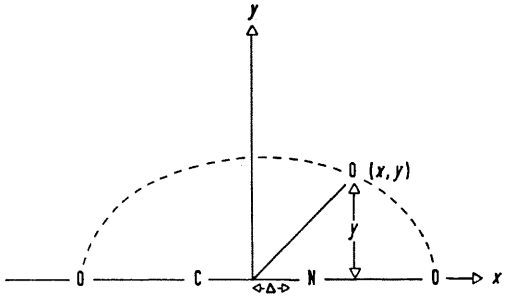

FIGURE 1. *Variables defining the rearrangement. The origin is at the midpoint of the* C–N *bond.* Δx *are the steps at which the total energy was calculated.*

All calculations were carried out at an IBM 360/91 computing system.

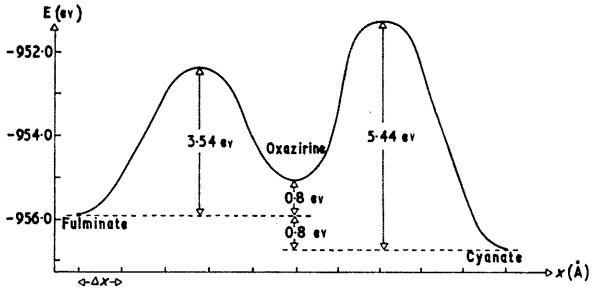

FIGURE 2. *Total energy as a function of* x, *minimized with respect to the* y *co-ordinates of the migrating oxygen atom.*

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[1] W. Beck, *Chem. Ber.*, 1962, **95**, 341.
[2] C. Grundmann and J. M. Dean, *J. Org. Chem.*, 1965, **30**, 2809.
[3] W. Beck and E. Schuierer, *J. Organometallic Chem.*, 1965, **3**, 55.
[4] E. L. Wagner, *J. Chem. Phys.*, 1965, **43**, 2728.
[5] G. W. Van Dine and R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 3227.
[6] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.
[7] A MINDO calculation of the problem according to the theory of N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 1969, **50**, 1269, was not successful because of convergence problems in the standard procedure, M. J. S. Dewar, M. Shanshal, and S. D. Worley, *J. Amer. Chem. Soc.*, 1969, **91**, 3590.
[8] K. B. Wiberg, *Tetrahedron*, 1968, 1083.
[9] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer Verlag, Berlin, 1966, p. 46.
[10] M. S. Gordon, *J. Amer. Chem. Soc.*, 1969, **91**, 3122.